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Purification of Glycerol Obtained during Biodiesel Synthesis and Production of Value - Added Product

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Abstract

Globally biodiesel is one of the best alternative fuels, and is seeing an exponential increase in demand. Despite the bright prospect of biodiesel production, efforts to commercialize it has been very limited. One of the major obstacles has been the high price associated with total production costs. Thus, it is necessary to reduce its processing cost to make biodiesel production feasible. This can be achieved by giving a value-added application for its byproduct. Glycerol is produced as an approximately 10-15% as a byproduct of the transesterification of triglycerides. Glycerol is a valuable byproduct obtained during biodiesel production but it is obtained in a crude form limiting its application. This byproduct needs to be purified efficiently to utilize it. Therefore, the present work aims to report phases in which the crude glycerol is purified. There are two phases in which the crude glycerol is purified. The Crude Glycerol is processed through saponification and then neutralization in the first phase. This produces three layers from which partly purified glycerol is obtained through separation. In the second phase of purification, the glycerol layer is separated from various salt impurities by the use of non-polar solvents. This glycerol is then extracted from the solvent and is subjected to decolorization using charcoal. Soaps and detergents are prepared as a value-added product from the obtained glycerol.

Keywords: *Biodiesel, Glycerol, Transesterification, Triglycerides, Value-Added Product*

1.0 Introduction

In the present days, it is seen that due to the more and more use of the fossil fuels they are getting depleted rapidly, hence the world is shifting to the best alternatives[1]. From the perspective of automobiles, biodiesel is chosen as one of the best alternative fuels. The production of this fuel is rapidly increasing all over the world as they are renewable, sustainable, cost-effective, and also gives lesser emissions compared to the available petroleum fuels[2]. Biodiesel is chemically known as mono-alkyl esters of long-chain fatty acids, which are derived by chemically reacting fats with alcohol like methanol or ethanol which in turn produces the methyl or ethyl esters which are commonly called biodiesel. This process is called the transesterification process[3]. In this process, the lipid sources or the fats which are chemically called triglycerides are converted into alkyl esters with the help of alcohols and in the presence of an acid or base catalyst[4]. The main sources of these lipids or fats are edible seed oils, dairy scum, animal fats, and non-edible seed oils. The commonly used edible seed oils are sunflower, soya bean, rapeseed, coconut, peanut, and

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palm oils[5]. Since these are edible foods, so the usage of these oils in the production of biodiesel may cause food scarcity and also leads to starvation in many developing countries. So due to the necessity of this edible oil as food non-edible seed oil is chosen as the best option for the production of biodiesel. This non-edible seed oils also have many greater advantages over edible seed oils, firstly these seeds are more readily available, and these crops can be easily cultivated even in low fertile lands with lesser costs, and also these seeds do not have many other applications. The most commonly used non-edible seeds are *Jatropha curcas*, *Pongamia pinnata*, *Madhuca indica*, Castor, Neem, Karanja, and Cotton seeds[6]. Based on the availability and cost we have chosen *Pongamia pinnata* oil for biodiesel production. Even though this biodiesel has many advantages but the production cost of this fuel is comparatively higher. So, it is necessary to reduce the cost of production. This can be achieved by giving the value-added application to its byproduct. The main by-product of biodiesel production is glycerol. But this obtained glycerol will be in the crude form, it is dark in color, has high pH, unpleasant odor and also has many impurities and salts which restrict its application. From the literature we know that around 10-15%wt of crude glycerol is produced during the production of the biodiesel[7], the impurities present in this crude glycerol are soap, salt, oil, free fatty acids, methanol, and spent catalysts[8]. But it is seen that the purified glycerol as more applications compared to crude glycerol. Hence, we are focused on the purification of this crude glycerol in order to provide a value-added application.

Glycerin is chemically known as the 1,2,3-Propanetriol[9]. This purified or refined glycerin has various applications in food industries where it is used as a humectant, sweetener, and also as a food preservative. This glycerin also contains antimicrobial and antiviral properties so it is seen in medical and pharmaceutical applications. It is also used in the making of soaps, facewashes and other personal care products due to its good moisturizing properties[10]. Whereas in the other hand the crude glycerol which is produced in biodiesel production which contains more impurities creates a significant challenge to convert them into value-added products. So, to avoid the market depletion of crude glycerol and to reduce the biodiesel cost production it is important to purify to the crude glycerol.

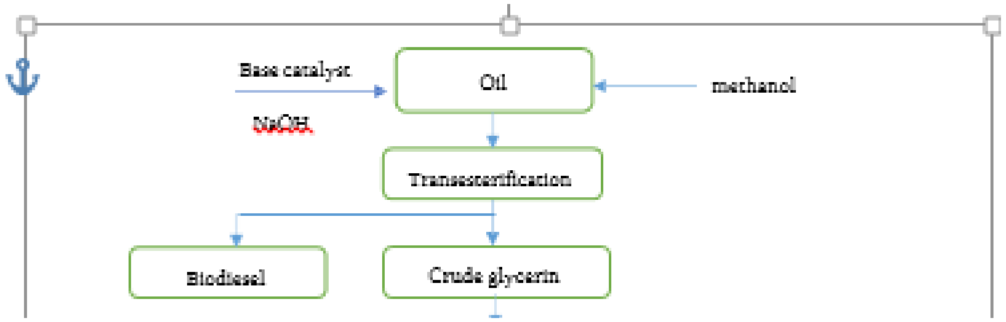
At present, there are many methods to purify glycerol like microfiltration, ultrafiltration, membrane filtration, ion exchange resin method, and vacuum distillation. With the help of these methods, a new method was synthesized to purify the crude glycerol into refined glycerin. It involves liquefication, saponification, neutralization, phase separation, removal of salts and impurities, decolorization, and vacuum distillation. Here we have conducted various trials on decolorization techniques to obtain the best result. At last, we compare this purified glycerin with the commercially available glycerin to validate our results.

2.0 Materials and Methodology

2.1 Materials

Crude glycerin of *Pongamia pinnata* oil which is obtained as the by-product of the biodiesel production by transesterification process is considered as the raw material for this research work and is taken from BRIDC, SIT, Tumakuru. The chemicals like Methanol (CH_3OH), isopropyl alcohol ($CH_3CHOHCH_3$), sodium hydroxide pellets (NaOH), and hydrochloric acid (HCl) are of lab grade and purchased from Vasa Scientific Co. Bengaluru for the experimentation purpose.

2.2 Methodology



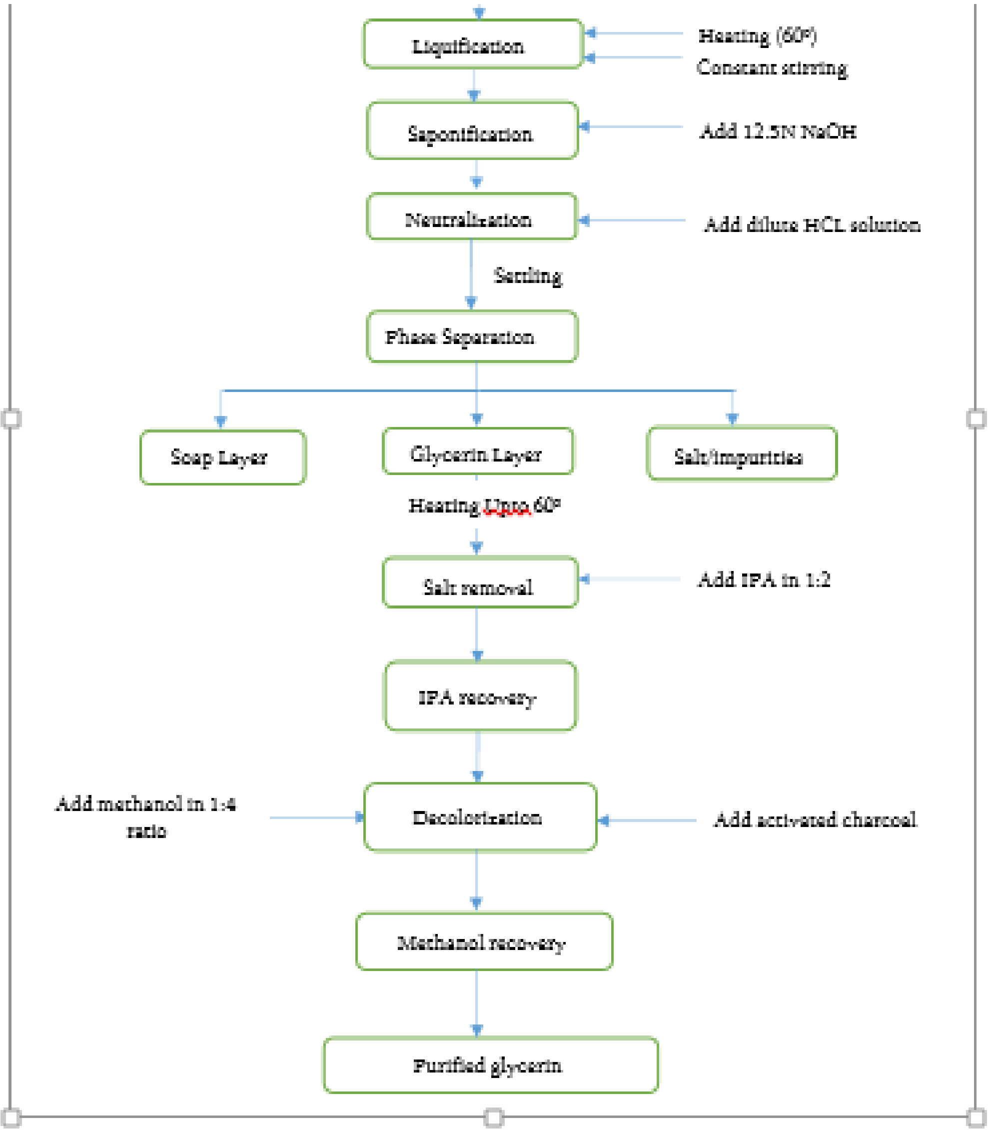


Figure 1. Flowchart of glycerin purification.

2.3 Glycerin Purification-Phase 1: Saponification, Neutralization and Phase Separation

Firstly, 1000ml of crude glycerin cake was taken and liquefied by heating up to 60^{0}C and stirred at a constant speed. After the complete liquefying of the crude glycerin then it is further subjected to the saponification process. This is done by adding 12.5N NaOH solution which is prepared by dissolving 100gm of NaOH pellets in 200ml of water. Here the remaining fatty acids in crude glycerin are converted into glycerin and soap. This process is carried out until the pH of the reaction mixture reaches 12 or 13 so to achieve complete saponification. Since, now the mixture is highly basic so to reduce its pH the mixture is subjected for neutralization. This is done by adding 1:1 diluted HCL solution to the mixture with constant stirring until the pH reaches around 7. Once it attains the neutral pH then it is subjected for settling for 4 hours to attain phase separation. Upon complete settling we get 3 layers, soap layer on the top, glycerin layer in the middle, and salt impurities layer at the bottom. Then the glycerin layer is separated and taken for the further purification process.

2.4 Glycerin Purification-Phase 2: Salt Separation and Decolorization

After the phase 1 purification, yellowish brown color glycerin layer is obtained. This glycerin still contains salts and colorizing compounds in it. So, the obtained glycerin layer is subjected for the second phase purification. In this phase, first the glycerin solution is heated up to 65^0C for 30 minutes allowed for 2 hours settling. Here, any presence of the methanol is evaporated as the boiling point of the methanol is 63.5^0C and remnants of the fatty acid soap chains and other impurities are settled at bottom and only the glycerin solution is decanted.

There are multitude of inorganic compounds due to saponification and neutralization in the first phase. Hence it is necessary to separate these. To do so, Isopropanol is used as a non-polar solvent. As such, glycerin dissolves in IPA whereas the other inorganic salts precipitate at the bottom. In this process, IPA is added in the ratio of 2:1 IPA to glycerin, and the solution is stirred at a constant rpm for two hours. It is then allowed to settle for 4 hours. The salts settle at the bottom of the settling funnel and glycerin is dissolved in the IPA. The solution of glycerin and IPA is then decanted and separated from the salts.

As now the IPA is completely dissolved in the glycerin, so it is required to separate the IPA from glycerin to use it. This is done by simple distillation, where the IPA-Glycerin solution is heated up to 85^0C as the boiling point of the IPA is 82.5^0C. After this process pure glycerin is obtained, even though most of the impurities have been removed, the color of glycerin obtained remains yellowish-brown in color, which prevents effective utilization. This solution is to be decolorized so that the obtained glycerin is colorless. The decolorization of this glycerin is done by adding 6.3gm of activated charcoal to the 100ml glycerin solution and the charcoal is removed by vacuum filtration technique. At last light yellowish colorless fluid is obtained. This appreciable result of the decolorization technique was obtained after conducting various trials.

3.0 Result and Discussions

Since the color of the glycerin was still yellowish brown in color, so to make this glycerin colorless, we have conducted various trials for the decolorization technique. The trials are discussed below.

3.1 Decolorization Trial 1

Here, activated charcoal is chosen as the decolorizing agent. 6.3gm of powdered activated charcoal is added to 100ml of glycerin. This mixture is stirred at a constant speed of 250 rpm for 2 hours. Then, this solution is subjected to centrifugation. In centrifugation, a temperature of 35^0C is set and the solution is split equally into two vials. The vials are placed in the opposite slots present in the rotor and the motor is set to rotate at 7000 rpm for 15 minutes. During centrifugation, the rotor rotates at the set speed. Due to centrifugal force, the denser particles settle at the bottom and less dense particles remain above. Upon centrifugation, the charcoal settles at the bottom of the vial due to higher density. The remaining glycerin is decanted from the charcoal.

3.2 Decolorization Trial 2

In this trial, the crystal form of charcoal is chosen for the decolorization technique. Because in the previous trial the result was little blackish yellow in color, here we are focused on the partial dissolving of the charcoal hence we took 6.3gm of crystal charcoal and mixed it with 100ml of glycerin by stirring at a constant speed of 200 rpm for 2 hours and then it is subjected for centrifugation for removing the charcoal.

3.3 Decolorization Trial 3

In this trial we have chosen the vacuum filtration technique for the charcoal removal, here we have added 6.3gm of powdered activated charcoal for 100gm of glycerin and mixed it by constant stirring. Then this glycerin charcoal mixture is subjected to a vacuum filtration technique. In vacuum filtration technique the pressure gradient created by the vacuum pump helps in separating the solute from solvent. And here we have chosen 2 grade 1 Whatman filter papers for filtration, this are placed above the porous plate of Bucher funnel to which the glycerin charcoal mixture is poured and above this filter paper a bed of Aluminum oxide ($Al2O3$) is added since it is a neutral compound it does not react with glycerin charcoal mixture and also does not allow the charcoal to settle on the porous plate. The purified glycerin is made to settle in Bucher flask.

3.4 Decolorization Trial 4

In this trial, we have chosen 2 decolorizing agents. One is activated charcoal and the other is methanol. Here, glycerin and methanol are mixed in a 1:4 ratio by stirring at a constant speed for around 30 minutes. Then 30gm of powdered activated charcoal is added for every 500 ml of the solution and it is constantly stirred for 2 hours to ensure proper mixing of charcoal. After this, the mixture is then subjected to vacuum filtration for removing the charcoal. The resulting solution which came from the vacuum filtration consists of both glycerin and methanol so to remove the methanol this mixture is subjected to rota-evaporation technique. Since the methanol is trapped inside the glycerin, so when compared to normal distillation here large surface of the heating mixture is exposed for evaporation and here the indirect heating of mixture takes place, as the mixture is placed inside a hot water bath so first the water gets heated above the boiling point of methanol after that the mixture gets heated and evaporated vapors of methanol are condensed and collected separately and refined glycerin is obtained at the last.

Table 1 shows the properties of the various glycerin samples and that compared to the properties of the commercially available glycerin. The density of the glycerin was calculated by measuring mass of the glycerin against considered volume. To measure the mass and volume of the glycerin, 25ml specific gravity bottle was taken and 25ml of glycerin sample was poured into that bottle and mass was measured and mass of the bottle was subtracted from this and divided with the volume considered. In the table it is seen that there is no much appreciable difference is observed in the density of all samples.

The transparency of the glycerin samples was measured by colorimeter. First the colorimeter was calibrated by placing the distilled water cuvette and black cuvette, after the calibration the small amount glycerin was taken in the cuvette and placed inside the sample compartment and wavelength was set to 490nm and meter set to the transparency mode and the data was recorded. From table we can say that the highest transparency was observed in trial 4 sample where 2 decolorizing agents are considered so that the maximum amount of the color absorption took place and charcoal was efficiently removed by vacuum filtration. Where the lowest transparency was observed in trial 2 sample because we have chosen crystal form charcoal so that only partial color absorption took place and centrifugation technique for the charcoal removal was not much efficient.

4.0 Conclusion

It is seen that the methodology adopted by us is efficient method to purify the crude glycerin into refined glycerin. From the results we can say that the trial sample 4, in which 2 decolorizing agents (4-part methanol for 1 part glycerin and 6 gm activated charcoal for 100 gm of solution) and subjected for vacuum filtration and rota-evaporation produces the most favorable properties. In this trial the finally obtained glycerin has a transparency of 95%, and relative density of 1.238. Hence there is negligible amount of difference between the obtained glycerin and that of commercially produced glycerin. This glycerin can be used commercially as a value-added product. Explosives production: Glycerol can be used as a humectant and plasticizer in explosives, improving their stability and performance. Glycerol-based dust suppressants are

Table 1. Measured properties of various glycerin samples

Properties	Units	Trial 1 sample	Trial 2 sample	Trial 3 sample	Trial 4 sample	Commercial glycerin
Density (mass/volume)	g/cm^3	1.231	1.227	1.233	1.238	1.261
Transparency at 490nm	Percentage (%)	71	52	83	95	100

effective in preventing dust generation during mining operations. Glycerol can be used as a flotation reagent in mineral processing, improving the separation of minerals from waste. Glycerol can be used as a lubricant in mining machinery, reducing friction and wear.

5.0 Acknowledgements

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